DOI: 10.1595/147106705X70291

Photography in Platinum and Palladium

PLATINUM & PALLADIUM PRINTING, SECOND EDITION

BY DICK ARENTZ, Elsevier, Focal Press, Boston, 2005, 234 pages, 65 Duotone plates
ISBN: 0-240-80606-9 (softbound), £27.99, €40.95

An Essay Book Review by Mike Ware
20 Bath Road, Buxton, Derbyshire, SK17 6HH, U.K.; E-mail: mike@mikeware.co.uk

Throughout its 166-year history, the technology of photography has been dominated by the photochemistry of silver halides. Their unique high sensitivity in development provides the only viable way of capturing a negative 'instantaneously' in the camera. But when it comes to printing from the 'black and white' negative to produce a monochrome positive, the brevity of exposure is not an important consideration, so the door is open to using other, less sensitive photochemical processes. Thus the exposure times used for printing can be lengthy and the printing-light sources intense. Throughout the history of photography, many alternative 'non-silver' printing processes have been devised in the quest to make images more permanent and artistically attractive than those provided by the silver media (1). Even in the dawn of photography, in 1839, Sir John Herschel stated:

> '*I was on the point of abandoning the use of silver in the enquiry altogether and having recourse to Gold or Platina*' (2).

The pioneers of the new art-science had already recognised that platinum could be an admirable image substance in its finely divided (nanoparticle) state. Platinum is far more inert than silver. In the polluted atmospheres of the Victorian industrial age, silver suffered from a serious vulnerability to sulfiding, which now accounts for the faded, pale brown look of many 19th century silver photographs (3).

However, it took another fifty years before a photochemical means of printing images in 'platinum black' was perfected by William Willis (4). It then became the preferred medium of leading photographic artists for a further three decades, until the Great War decreed that platinum was a strategic material for catalysing the manufacture of explosives, and its frivolous use for photography and jewellery was banned.

This put a temporary halt to the production of commercial platinotype paper, but Willis responded by devising a palladium printing paper. Such noble metal processes depend on the photochemistry of iron(III) polycarboxylates, which have a light sensitivity so low that one can only make contact prints from same-sized negatives, necessitating the use of large format cameras. Eventually, the competition with more sensitive silver halide papers, produced in response to the need for enlarging miniature camera negatives, led to Willis's Platinotype Company being wound up in 1937 (5).

When image quality and archival permanence are paramount considerations, the prime alternative to silver printing still remains the platinotype, and analogous palladiotype. Since the 1970s dissatisfaction with the commercial silver-gelatin printing 'monoculture' led some photographic artists, especially in the U.S.A., to rediscover the 19th century method of platinotype, and to coat their own sensitised papers with solutions of the appropriate chemicals: iron(III) oxalate and potassium tetrachloroplatinate(II) (6).

The Book

The Focal Press book, "Platinum & Palladium Printing", Second Edition, by Dick Arentz describes itself as '*the only comprehensive work*' on this subject, and so commands our serious attention. This book is not a history (7) nor yet a chemistry (8) of the process, for which the reader must look elsewhere. Arentz's treatise is intended as a practical manual of instruction, providing a fully detailed account of one method of accomplishing palladium-platinum prints, and of creating the large

Plate 1.1 from the Second Edition of Dick Arentz's book "Platinum & Palladium Printing", entitled 'Levens, England. 2000 12 × 20 inch Pd.' The image colour, a rich yellowish-brown, is characteristic of a developed palladium print

photographic negatives that are the prerequisites. The only rival sources of published instruction in these skills, which are admittedly briefer, can be found within multi-topic works on what has come to be called 'alternative' photography (9).

Traditional Palladium-Platinum Printing

Arentz is the master-craftsman leading the school of traditional palladium-platinum printing in the U.S.A. The technical content of his book is visually leavened by duotone plates exemplifying his own exquisite landscape images, which were executed originally in the giant format of 12" × 20". His workroom equipment, resources, and practices are minutely delineated in Chapter 2, 'Setting Up a Laboratory', and provide a counsel of perfection for all practical workers in this arena. This book will therefore appeal chiefly to advanced photographic print-makers, especially those accustomed to large format practice, who are competent in the control of exposure and development to achieve precalibrated density parameters, as exemplified by Ansel Adams's celebrated Zone System. The sensitometry of photographic materials, measured by step-tablet testing and plotting the characteristic curves of optical density versus log(relative exposure), is the mainstay of this work; so any readers unfamiliar with these concepts may find themselves a trifle challenged.

In view of the author's concern for technical precision, it is a reviewer's melancholy duty to report some rather unfortunate errors. Chapter 3 on 'The Negative' deals with photographic sensitometry, but when it comes to explaining logarithms and their relationship to photographic stops, it makes at least five mistakes in elementary mathematics in the space of half a page: for instance, a density of 4.0 is not equivalent to 100 stops, as stated, but 13.3 stops. Likewise, the chemically-literate reader will be distressed to see in Chapter 4, on 'Chemicals', formulae written as $K_2CR_7O_7$ (for potassium dichromate), $K_2C_2O_2$ (for potassium oxalate), and $C_6H_5NA_3$ (for sodium citrate), among others, which are solecisms as uncomfortable to a chemist's eye as spelling errors to a reader, and which will not inspire confidence.

Paper

While all the other printing parameters are controllable, the paper substrate remains the last great imponderable in hand-crafted platinum-palladium

Commercial platinum print ca. 1900, by 'C&P', photographer unknown, entitled "Wells Cathedral, Nave looking East". The image colour, neutral grey-black, is typical of a 'cold-developed' platinotype of the period

processes, since the constituents of the sensitiser are in intimate contact with any additives in the paper that may prove hostile and inhibiting to the chemistry. In the mid 1980s, mainly for environmental and conservation reasons, the methods of industrial paper manufacture underwent a profound change. However, the new papers produced – while admirable for other purposes – did not suit the platinum printer. Chapter 5 on 'Paper' carries a useful survey of tests on many commercial 'fine art' papers now available in the U.S.A., and reviews their suitability for palladium-platinum printing, and how problems with them may be overcome by acidification.

In Chapter 6, 'The First Print', the reader will discover how to make a palladium print – but only provided that the reader has purchased a particular chemical kit (10). This is because the instructions in this book are wedded to the products of a particular U.S. supplier of pre-packaged chemical solutions for palladium-platinum printing. While this may be a convenient dependency, it may ultimately limit the book's usefulness.

Chapter 7, 'Choose Your Method', is not as wide in scope as it sounds, being solely concerned with the method of contrast control in the print. If the extensive advice about the correct making of negatives were to be followed in the first place, much of this Chapter would be superfluous. Chapter 8, on 'Calibration', provides more instruction in controlling print contrast, and Chapter 9, 'The Platinum and Palladium Print', describes the *modus operandi* of coating paper, exposure to ultraviolet light, and processing.

Chapter 10 on 'Advanced Technique' describes the effects of humidity, variations in the developing procedure, and the finishing of prints, and Chapter 11, 'Problems', is, unsurprisingly, on troubleshooting.

The remaining half of the book (116 pages) is devoted almost entirely to negatives and sensitometry. This is aimed at precisely matching the optical density range of the negative to the logarithmic exposure range of the process. Thus Chapter 12 is about 'The Film and Paper Curves', and lastly Chapter 13 is about 'Using the Print Curves'. After

this are seven Appendices, mainly concerned with the making of suitable large format camera negatives. The most useful inclusion here is by 'guest author' Mark I. Nelson, describing: 'Crafting Digital Negatives for Contact Printing Platinum and Palladium'. This topic is becoming of increasing importance as digital imaging takes hold and film manufacturers withdraw their traditional silver-gelatin materials from the market.

Monochrome Image Colours

The colour of the monochrome image is an issue of primary importance to photographic artists. It depends both on the metal and the method. If the duotone plates of the book accurately reproduce Arentz's original palladium-platinum prints, then the predominance of palladium in his *modus operandi* coupled with the use of a development process would seem to result in characteristically yellowish-brown images. This may not satisfy all tastes. The neutral 'engraving' black so esteemed in the traditional platinum print is not seen here, nor even the rich purplish browns of 'sepia platinotype'. Indeed, it appears that the working methods that Arentz and his suppliers have now evolved cannot readily furnish pure platinum prints of good quality – a failing which is partly attributed to the constitution of modern commercial art papers.

It is true that a fine print in palladium is much easier to make than one in platinum, because platinum(II) salts are more reluctant to be reduced to platinum metal, which can cause poor image quality, so the former is strongly recommended to newcomers in this field (10). Indeed, some readers may recognise the origin of this problem: that the chemical kinetics of complexes of a 3rd row transition metal like Pt are generally slower than those of a 2nd row metal like Pd, due to larger crystal field activation energies, resulting from the spatial extent of the *d*-orbitals. Thus the more labile Pd(II) complexes are easily reduced to the metal by Fe(II).

It is regrettable – and some readers of this Journal may think it unprofessional – that this current practice should be referred to by many as 'platinum printing', when the product usually chiefly consists of palladium. In comparing the use of these two noble metals for photography, there are also the considerations of cost and safety. Palladium is usually much less expensive than platinum, but readers will know that there have been some wild market price excursions in the past (due to speculation) which have sent shock waves through the printing community.

A health and safety view of the metal salts, omitted from Arentz's book, is that chloro-complexes of platinum(II), unlike those of palladium(II), have a marked biological activity, and constitute a human allergenic hazard. This was first discovered in 1911 through cases of industrial illness arising among workers in an early platinotype paper factory.

Indeed, while the illustrations in both editions of Arentz's books indicate that very fine palladium-platinum prints may be made by the hands of a master who is prepared to take limitless technical pains, the reader may wonder if this is the only possible route to success. The second edition now omits any account of an alternative method which he briefly described in his first edition, namely, a modern 'print-out' method of platinum-palladium printing, employing a slightly different photochemistry. It seems fair to redress this imbalance by comparing the two below.

Development Printing versus the Print-out Process

The ills of the traditional method stem from the chosen photosensitive iron(III) salt: ferric oxalate. This is a notoriously wayward and ill-characterised substance; the nature of the product, which is evidently capable of extensive polymorphism, varies with its method of preparation. An indication of the difficulty of manufacture is apparent from its commercial price: iron(III) oxalate costs over 100 times as much as iron(II) oxalate! It is obtained as an amorphous solid, seemingly not crystallisable, and in consequence its structure has not been determined by X-ray diffraction. It is hard to dissolve in water without an additional ligand, and the aqueous solution undergoes changes in its properties over time, to the extent that scrupulous workers (as we learn from Arentz's Appendix G)

prefer to make up a fresh solution each night before printing.

The photochemistry of iron(III) oxalate may be represented approximately thus:

$$Fe_2(C_2O_4)_3 \xrightarrow{h\nu} 2FeC_2O_4\downarrow + 2CO_2\uparrow$$

The photoproduct, iron(II) oxalate, is highly insoluble and cannot reduce platinum(II) or palladium(II) salts to metal, unless it is solubilised by complexation, for example, with oxalate ions:

$$[PtCl_4]^{2-} + 2FeC_2O_4 + 4C_2O_4^{2-} \rightarrow Pt\downarrow + 4Cl^- + 2[Fe(C_2O_4)_3]^{3-}$$

Hence the traditional 'development' process of platinum and palladium printing, which calls for a processing bath of hot potassium oxalate solution, or similar ligand, to bring out the metal image in the exposed paper.

However, there is an accessible alternative for the light-sensitive ingredient: ammonium iron(III) oxalate. This is a well-characterised, highly crystalline, analytically pure substance, of known molecular structure. It is universally available at low cost, and dissolves very readily to give a stable aqueous solution. Moreover, its photochemistry leads to a 'print-out' process, as follows:

$$[Fe(C_2O_4)_3]^{3-} \xrightarrow{h\nu} [Fe(C_2O_4)_2]^{2-} + 2CO_2\uparrow$$

The iron(II) photoproduct in this case is already a soluble complex, so if the sensitised paper contains sufficient water molecules, as will be the case for any cellulose paper exposed to ambient relative humidity of 70- 80%, the ions can mobilise immediately to reduce the platinum metal *in situ*:

$$[PtCl_4]^{2-} + 2[Fe(C_2O_4)_2]^{2-} \longrightarrow Pt\downarrow + 4Cl^- + 2[Fe(C_2O_4)_2]^-$$

Thus a 'print-out' process results, in which the final image is formed substantially during the light exposure, and no 'development' bath is required, simply 'clearing' baths to remove the excess soluble chemicals. This enables a *modus operandi* quite different from the traditional method, and more economical in time, effort, and materials. Images may be printed satisfactorily 'by inspection', without prior calibration (11). The print-out process is 'self-masking', in that the blackening of the shadow tones inhibits their further darkening by light, so a long density range in the negative may be accommodated, and the control of contrast is more relaxed. By regulating the relative humidity of the paper before exposure, better image colours result with palladium, because the metal nanoparticles are allowed to grow larger, and can furnish even a neutral black. Provided that a suitable paper substrate is chosen, the method can also yield an excellent print in pure platinum.

In conclusion, it might be observed that, for many artists, the intrusion of technical minutiae into the creative workflow can tend to inhibit their endeavours. If the science can be predesigned to work as transparently and unobtrusively as possible, so much the better for art.

Artists deserve the best science.

References

1 M. J. Ware, 'Noble Metals for Common Images', in "Photochemistry and Polymeric Systems", eds. J. M. Kelly, C. B. McArdle and M. J. de F. Maunder, Special Publication No. 125, Royal Society of Chemistry, Cambridge, 1993, pp. 250-265; http://www.mikeware.co.uk/mikeware/Ironic_Manifesto.html

2 L. J. Schaaf, "Out of the Shadows: Herschel, Talbot and the Invention of Photography", Yale University Press, New Haven & London, 1992

3 M. Ware, "Mechanisms of Image Deterioration in Early Photographs: The Sensitivity to Light of W. H. F. Talbot's Halide-Fixed Images 1834-1844", Science Museum and National Museum of Photography, Film & Television, London, 1994

4 M. Ware, 'The Eighth Metal: the Rise of the Platinotype process', in "Photography 1900", eds. J. Lawson, R. MacKenzie and A. D. Morrison-Low, National Museums of Scotland, Edinburgh, 1994, pp. 98-111; http://www.mikeware.co.uk/mikeware/Eighth_Metal.html

5 For the early history of platinotype, readers are referred to: I. E. Cottington, 'Platinum and Early Photography', *Platinum Metals Rev.*, 1984, **28**, (4), 178; see also: D. E. Webster, 'Noble Metals in Photography', *Platinum Metals Rev.*, 1987, **31**, (3), 124

6 G. Tice, 'Durable Beauty in Images of Platinum', in "Caring for Photographs", Life Library of Photography, Time-Life Books, Alexandria, Virginia, 1972, pp. 86–93

7 L. Nadeau, "History and Practice of Platinum Printing", Atelier Luis Nadeau, New Brunswick, Canada, 1994

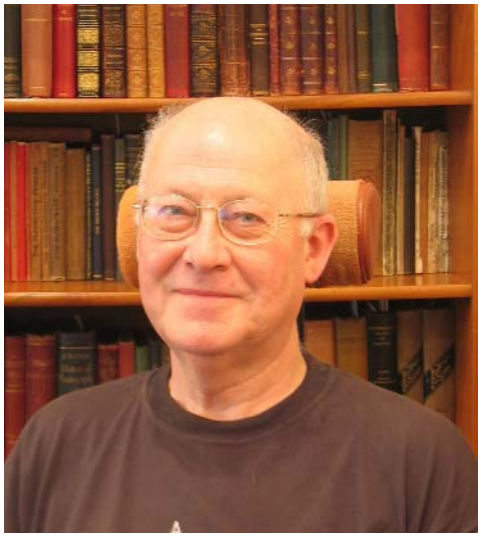
8 M. J. Ware, 'An Investigation of Platinum and Palladium Printing', *J. Photogr. Sci.*, 1986, **34**, 165; http://www.mikeware.co.uk/downloads/Palladium_Printing.doc

9 R. Farber, "Historic Photographic Processes", Allworth Press, New York, 1998; C. James, "The Book of Alternative Photographic Processes", Delmar, Thomson Learning, New York, 2002

10 Maker/Supplier: Bostick & Sullivan, Santa Fe, New Mexico, U.S.A., http://www.bostick-sullivan.com/; Supplier: Photographers' Formulary, Inc, Condon, Montana, U.S.A., http://www.photoformulary.com/

11 M. Ware, 'Platinum Reprinted', *Br. J. Photogr.*, 1986, **133**, (41), 1165; M. Ware, *Br. J. Photogr.*, 1986, **133**, (42), 1190; P. Malde, 'New Solutions for Platinum Printers', *View Camera*, September/October, 1994, 36-41; http://www.mikeware.co.uk/mikeware/Platino-Palladiotype.html

The Reviewer



Dr Michael J. Ware is a chemist with a D.Phil. in spectroscopic research from the University of Oxford. Following an academic career at the University of Manchester, (Honorary Fellow), he now independently studies the history, science, art and conservation of 'alternative' photographic processes. His work on printing in noble metals, especially gold, platinum and palladium, was awarded the Hood Medal of the Royal Photographic Society. He is a consultant to the National Museum of Photography, Film and Television, and has supervised postgraduate research in photograph conservation at the Victoria & Albert Museum and the Royal College of Art, and in alternative photographic processes at the University of Derby. He exhibits his own photographic work widely, and conducts workshops in the U.K. and U.S.A. His research is published in popular and academic scientific and photographic literature, such as *History of Photography*. He has published books on Talbot's photogenic drawing process (1994) and Herschel's cyanotype process (1999). His books on Herschel's chrysotype – photography in gold – are due out shortly.
His website is: http://www.mikeware.co.uk/